

**Temporal changes in the
concentrations of zinc
and cadmium in the
sedimentary strata of
Nozha Hydrodrome,
Alexandria, Egypt**

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KEYWORDS

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Abstract

This study is concerned with the temporal changes in the levels of zinc and cadmium in the sediments of Nozha Hydrodrome during the past 100 years. Seven sediment core samples, covering the study area, were collected from the bottom of the Hydrodrome. A five-step sequential extraction technique was applied to determine the solid phase concentrations of zinc and cadmium. Zinc gives an idea of the quantities of sewage effluents, while cadmium provides an indication of the amounts of agricultural discharges. The vertical distribution curves show that the average total concentrations of zinc in the sediments increased at a rate of $2.5 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1900 to 1950 and at $1.5 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1950 to 1990. Since 1990 the zinc concentration in Nozha Hydrodrome sediments has been decreasing at $1.5 \mu\text{g g}^{-1} \text{y}^{-1}$. The average total cadmium concentration exhibits a different vertical distribution pattern: it increased at a rate of $0.42 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1900 to 1950, after which it became constant from 1950 to 1970. Since 1970 it has been increasing at $0.53 \mu\text{g g}^{-1} \text{y}^{-1}$. The ongoing increase in cadmium concentrations in the sediments is due to the increase in agricultural discharges into the Hydrodrome, especially as significant amounts of phosphate fertilizers are used to nourish the soil around the Hydrodrome. The rise in cadmium concentrations since 1900 has been accompanied by a similar increase in zinc concentrations with time resulting from

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the discharge of untreated sewage into the Hydrodrome. In 1990 a sewerage system and sewage treatment plant came into operation, as a result of which discharges of domestic effluent into the Hydrodrome ceased. Since then the amount of zinc in sediments has been decreasing steadily.

1. Introduction

The levels of heavy metals in sediments reflect the impacts of industrial, agricultural and urban development (Fang et al. 2005). They tend to be trapped in sediments of aquatic environments, and their concentrations in particulate form are much higher than those in dissolved form (Balls 1989, Comber et al. 1995). Although, under certain circumstances, part of the metals accumulated in this way may be subsequently released to the overlying water by either physical disturbance (Boughriet et al. 1992) or diagenesis (Petersen et al. 1995), the majority of the accumulated metals remain in the sedimentary compartment. Therefore, the sediment strata at the bottom of an aquatic environment represent a time record (pollution history book) of human activities in that area.

Studies of heavy metals in the environment are important for two main reasons: public health and environment. In the former, attention is drawn to the necessity of measuring the accumulation of heavy metals, particularly those which pose serious health hazards to humans, such as cadmium. In the latter, the main problem is to prevent biological deterioration and to identify the sources that threaten the ecological equilibrium. In this regard, the more abundant heavy metal zinc may sometimes represent a greater hazard than cadmium (Kinne (ed.) 1984).

The present study is concerned with the temporal variation in the concentrations of two specific heavy metals, zinc and cadmium, since they are strongly influenced by anthropogenic inputs (Scoullou & Constandianos 1996). However, despite their importance, data on metal concentrations in Nozha Hydrodrome, until recently, have been very scarce. To our knowledge, no systematic report has been published on the temporal variation of those metals in Nozha Hydrodrome sediments. The aim of this work, therefore, was to investigate the temporal variation in the concentrations of zinc as an indicator of urban activities and cadmium as an indicator of agricultural activities in the sediments of Nozha Hydrodrome.

2. Study area

Nozha Hydrodrome (latitude 31.193°N, longitude 29.977°E) is located south of Alexandria City (Figure 1). It is an enclosed, nearly circular freshwater body with a surface area of about 5.5 km² and an average water depth of 2.1 m. The Hydrodrome water has an average salinity ranging

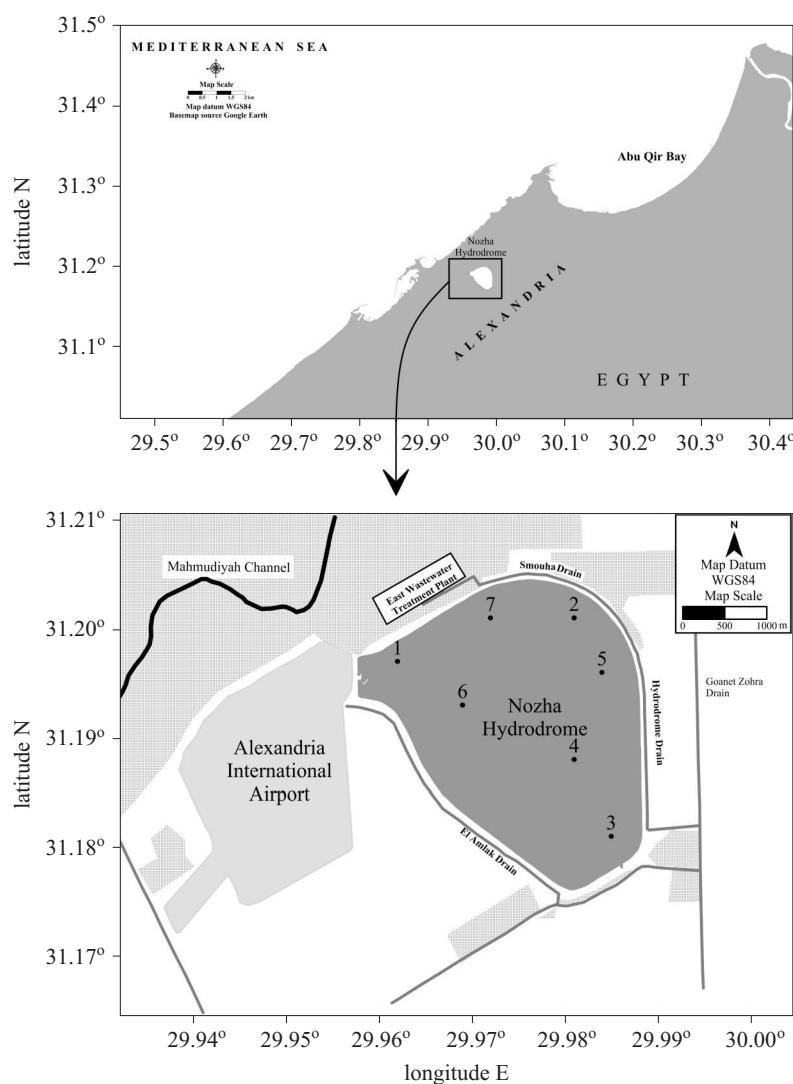


Figure 1. Nozha Hydrodrome and the surrounding features; white areas – cultivated land, crosshatched areas – residential zones, grey lines – drains

between 1.2 and 2.9, and an average pH of 8.9 (Youssef & Masoud 2004). The water temperature fluctuates between 15°C in December and 33°C in August (Ahdy & Saad 2006). It used to be part of Lake Maryut, which received its fresh water from the Mahmoudiyah Channel through a small feeder canal. In 1939, the Hydrodrome was isolated completely from Lake Maryut by a steep-sided concrete embankment. Later the Hydrodrome was used as a fish culture and a duck breeding farm. After the Mahmoudiyah Channel had ceased to flow, the Hydrodrome received its water through

several drains that poured untreated domestic and agricultural effluents into the pond (Moustafa et al. 2009). The surplus water of the Hydrodrome is discharged via an outlet located at its south-western limit to the El-Amlak drain that pours into Lake Maryut (Ahdy & Saad 2006).

3. Material and methods

A hand auger equipped with a polyethylene tube was used by SCUBA divers to collect seven sediment core samples, each approximately 75 cm in length, from the bottom of Nozha Hydrodrome (Figure 1). The polyethylene tubes containing the sediments were kept in ice boxes and transferred to the laboratory for analysis. Based on the average sedimentation rate (0.65 cm y^{-1}) in Nozha Hydrodrome (determined by Ahdy (1982) using in situ sedimentary traps) the core samples were split into subsamples, each one representing ~ 5 years of sedimentation (approximately 3.25 cm). A total of 23 sediment subsamples were obtained for each core. The concentrations of zinc and cadmium in the bulk sediment subsamples were extracted using a technique modified from Tessier et al. (1979), Steinberg & Tayarani-Dastmalian (1993) and Perin et al. (1997). Measurements of zinc and cadmium concentrations were carried out using an Atomic Absorption Spectrophotometer (Perkin Elmer Analyst 800, equipped with Zeman background correction). To ensure the accuracy of these concentrations, the above procedure was conducted 5 times on standard reference material. The recoveries were 90% for Cd and 110% for Zn. The precision of the technique was tested by replicate analysis of the studied metals, using IAEA-SL-1 Standard Reference Material (International Atomic Energy Agency), as shown in Table 1.

Table 1. Replicate analysis for IAEA-SL-1 Standard Reference Material

IAEA-SL-1	Cd = 0.26 [μg^{-1}]	Zn = 223 [μg^{-1}]
run 1	0.31	231
run 2	0.27	228
run 3	0.28	225
run 4	0.25	220
run 5	0.24	235
mean	0.27 ± 0.025	227 ± 5.7
coefficient of variation [%]	9.26	2.51

To test the reliability of the dating calculation using the sedimentation rate, the data on the total concentrations of zinc and cadmium in the sediments in the years 1977 (Ahdy 1982, 1987, El-Rayis & Saad 1990) and

2004 (Ahdy & Saad 2006) were plotted on the vertical distribution curves together with the data of the present study.

4. Results

Because of the homogeneity and similarity of the sediment core lithology, the data of the seven cores have been averaged to obtain an overview of the variation of zinc and cadmium concentrations with time for the entire Hydrodrome.

The average vertical distributions of zinc and cadmium concentrations in the solid phases (exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter, and residual) and the average total concentrations in core sediments of Nozha Hydrodrome are presented in Figures 2 and 3 respectively.

Zinc concentrations in the exchangeable and carbonate phases in the sediment core are much lower than those in the other phases, whereas the oxide-phase concentrations are the highest (Figure 2). The zinc

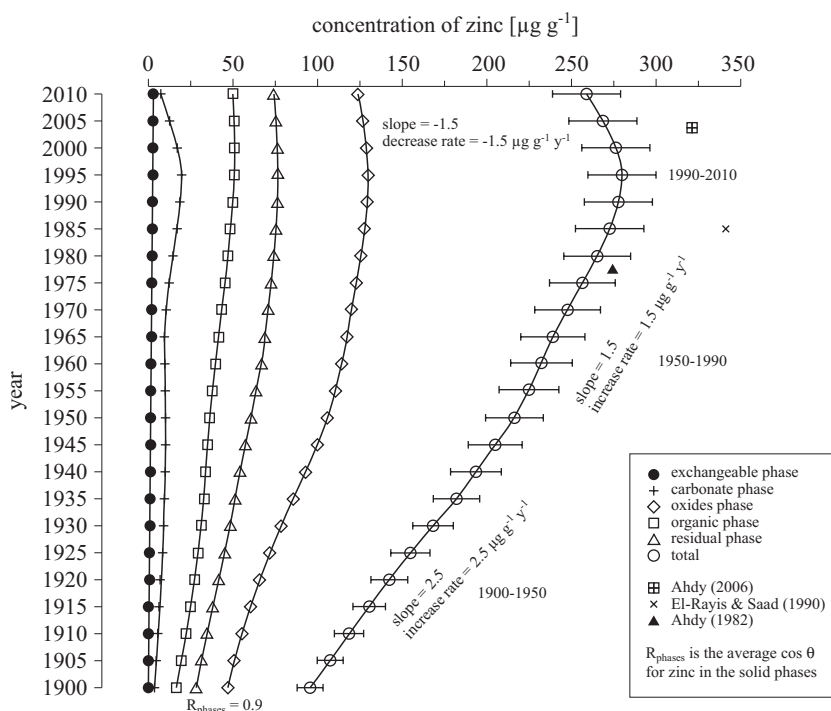


Figure 2. Vertical changes with time in the concentrations of zinc phases in the sediments. R_{phases} is the average $\cos(\theta)$ for zinc in the solid phases (see text for details)

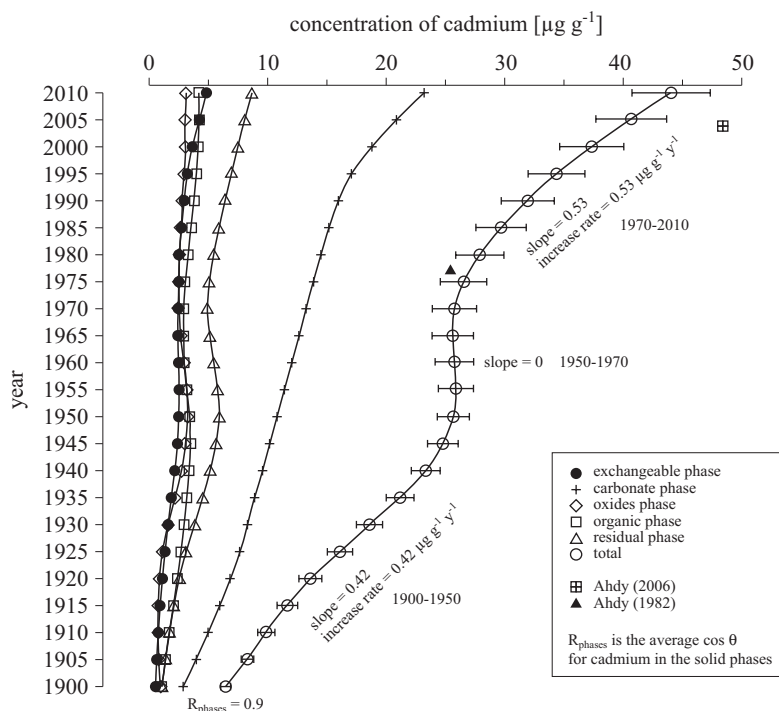


Figure 3. Vertical changes with time in the concentrations of cadmium phases in the sediments. R_{phases} is the average $\cos(\theta)$ for cadmium in the solid phases (see text for details)

concentration in the sediments was at a minimum ($96.2 \mu\text{g g}^{-1}$) in 1900 and reached a maximum ($280 \mu\text{g g}^{-1}$) in 1990. The rate of increase in the total zinc concentrations with time was $2.5 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1900 to 1950, decreasing to $1.5 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1950 to 1990. Since 1990 the total zinc concentration has been decreasing at a rate of $1.5 \mu\text{g g}^{-1} \text{y}^{-1}$, reaching $258.8 \mu\text{g g}^{-1} \text{y}^{-1}$ in 2010.

Cadmium concentrations are higher in the carbonate phase than in the other solid phases (Figure 3). The variation in the total cadmium concentrations (min = $6.5 \mu\text{g g}^{-1} \text{y}^{-1}$ in 1900, max = $43.8 \mu\text{g g}^{-1} \text{y}^{-1}$ in 2010) with time shows a different pattern. The average total cadmium concentration increased at a rate of $0.42 \mu\text{g g}^{-1} \text{y}^{-1}$ from 1900 to 1950, after which there followed a period of approximately no variation (constant concentrations of $26 \mu\text{g g}^{-1} \text{y}^{-1}$) from 1950 to 1970. After 1970 the average total cadmium concentrations in the sediments increased at a higher rate ($0.53 \mu\text{g g}^{-1} \text{y}^{-1}$) than during the period 1900–1950. The data also show that the vertical distribution curves for both zinc and cadmium follow the same pattern for each metal separately.

5. Discussion

The data on the concentrations of total zinc and cadmium in the surface sediments of Nozha Hydrodrome in 1977 (Ahdy 1982), 1987 (El-Rayis & Saad 1990) and 2004 (Ahdy & Saad 2006) well match those obtained in this study at depths in the sediment cores representing similar years (Figures 2 and 3). This indicates that the technique of dating the Nozha Hydrodrome sediment cores based on the sedimentation rate calculations used in this study is quite reliable. On the other hand, comparison of the average zinc ($258 \mu\text{g g}^{-1}$) and cadmium ($43 \mu\text{g g}^{-1}$) concentrations in the upper layer of the sediment cores with those in the surface sediments of the Nile Delta Lakes Maryut (zinc = $508 \mu\text{g g}^{-1}$, cadmium = $27 \mu\text{g g}^{-1}$) (Saad & Ahdy 2006), Burullus (zinc = $217 \mu\text{g g}^{-1}$, cadmium = $5 \mu\text{g g}^{-1}$) and Manzala (zinc = $432 \mu\text{g g}^{-1}$, cadmium = $84 \mu\text{g g}^{-1}$) (Saeed & Shaker 2008) shows that zinc in Nozha sediments is lower than in its mother Lakes Maryut and Manzala, whereas it is slightly higher than in L. Burullus; the cadmium concentration is higher in Nozha sediments than in Lakes Maryut and Burullus but lower than in L. Manzala. These variations in the concentrations of both zinc and cadmium in the surface sediments of the Nile Delta lakes indicate their dependence on the source that supplies both metals to them.

The history of zinc and cadmium concentrations in the sediments of Nozha Hydrodrome shows that there was an increase in zinc from 1900 to 1990 followed by a decrease from 1990 to 2010. On the other hand, since 1900 cadmium concentrations in the sediments have been rising continuously. The zinc concentration in the natural sediments of aquatic environments is $\sim 120 \mu\text{g g}^{-1}$ or less (CEQG 1999, ANZECC & ARMCANZ 2000, WDNR 2003) and any increase over this value points to increased input due to human activities. In 1900 the total concentration of zinc in Nozha Hydrodrome sediments was $96.2 \mu\text{g g}^{-1}$. This value is below the level of zinc in natural aquatic sediments, and the Hydrodrome was considered a clean environment. At that time, there were no urban areas around the Hydrodrome and no untreated sewage was dumped into the pond. The higher zinc concentrations were due to the increase in the untreated domestic effluents discharged into the Hydrodrome as a result of the progressive urbanization around it. Two periods can be distinguished: one was from 1900 to 1950, when the annual rate of increase in total zinc in the sediments was $2.5 \mu\text{g g}^{-1} \text{ y}^{-1}$, and the other from 1950 to 1990, when the annual rate of increase of zinc in the sediments fell to $1.5 \mu\text{g g}^{-1} \text{ y}^{-1}$. Several authors relate the elevated zinc concentration in sediments to anthropogenic discharges to the aquatic environment (Zhu et al. 2001, Taylor & Kesterton 2002, Bi 2003, Dassenakis et al. 2003, Wu et al. 2004, Dong et al. 2004, Yuan et al.

2004, Abd El-Azim & El-Moselhy 2005, Saad & Ahdy 2006, Huang et al. 2007, Luo et al. 2008). As long as Nozha Hydrodrome received untreated sewage from the surrounding urban areas, the rise in zinc concentrations in the sediments reflected the progressive expansion in urbanization with time during the period from 1900 to 1990.

In 1990, the municipality of Alexandria city completed the construction of the Nozha district sewer system and the new East Wastewater Treatment Plant (EWTP) that serves the southern and western districts of the city. After the implementation of the sewer system and sewage treatment plant, much of the discharge of untreated domestic effluents to Nozha Hydrodrome stopped (WWCG 1992). Since then, and despite the ongoing urbanization around the Hydrodrome, the zinc concentration in the sediments has been decreasing at a rate of $1.5 \mu\text{g g}^{-1} \text{y}^{-1}$.

The point of determining the concentrations of zinc and cadmium in the mobile and residual phases was to assess the stability of the studied metals in the solid phase. The similar vertical distribution patterns (temporal behaviour) for the concentrations of the metals in the different phases indicate that there is a slow or probably no mobilization with time and that the metals tend to be trapped in the solid phase. By contrast, an insignificant relationship indicates mobilization of the metal from the solid to the dissolved phase. To test the potential mobilization from sediment to water the average cosine θ coefficients (R_{phases}) for zinc and cadmium were calculated. This measure represents the relationship between the mobile phases and the residual phase of a metal with time.

The average R_{phases} for zinc concentrations in sediment is 0.9 (Figure 2). This highly significant relationship, together with the environmental conditions prevailing in Nozha Hydrodrome – $\text{pH} = 8.9$ (Youssef & Masoud 2004) and $\text{DO} = 6.02 \text{ mg l}^{-1}$ (Saad & Safty 2004) – suggests that zinc tends to be trapped in the sedimentary compartment. This interpretation could also be inferred from the similarity of the patterns of the vertical distribution curves for zinc in the different phases (Figure 2). Moreover, the average concentration of dissolved zinc in Nozha Hydrodrome water is $8.1 \mu\text{g l}^{-1}$ (Saad 1987). Comparing the zinc concentration in water with that of natural surface water ($10 \mu\text{g l}^{-1}$) (Calamari & Naeve (eds.) 1994) indicates that Nozha Hydrodrome water is of good quality and confirms that most of the zinc reaching the Hydrodrome is accumulated and retained in the sediments.

The variation in cadmium concentrations with time in Nozha Hydrodrome sediments exhibits a different pattern. Since 1900 the concentration of cadmium in Nozha Hydrodrome has been high ($6.5 \mu\text{g g}^{-1}$) as a result of agricultural wastewater discharges into the pond. During the period from 1900 to 1950 the concentration increased at a rate of $0.42 \mu\text{g g}^{-1} \text{y}^{-1}$.

Between 1950 and 1970 cadmium concentrations apparently did not change, but in 1970 the rate of increase ($0.53 \mu\text{g g}^{-1} \text{y}^{-1}$) became faster than that of 1900–1950. The soil of the cultivated land surrounding the Hydrodrome is fertilized with phosphate and nitrate, and fertilizers produced from phosphate ores constitute a major source of diffuse cadmium pollution (Calamari & Naeve (eds.) 1994). The strong relationship between cadmium and fertilizers has been reported from many areas, e.g. in soil samples collected from Alberta, Manitoba and Saskatchewan, Canada (Lambert et al. 2007). Taylor (1997) mentioned that the increase of cadmium in New Zealand sediment samples is associated with the application of phosphate fertilizers and that over 80% of the Cd added to phosphate fertilizers has remained in the topsoil. The stabilization of cadmium in sediment is enhanced by alkaline pH and high dissolved oxygen concentrations (Thawornchaisit & Polprasert 2009). The cadmium concentration in the water of Nozha Hydrodrome is $0.2 \mu\text{g l}^{-1}$ (Saad 1987). This value is lower than that of cadmium in natural water ($\sim 1 \mu\text{g l}^{-1}$), as reported by Calamari & Naeve (eds.) (1994). The solubility of cadmium in water is influenced to a large degree by its acidity; suspended or sediment-bound cadmium may dissolve when there is an increase in acidity (Ros & Slooff (eds.) 1987). At present, the high pH and dissolved oxygen concentrations of Nozha Hydrodrome water do not permit mobilization of cadmium from the solid to the dissolved phases, so it accumulates with time in the bottom sediments. The calculated R_{phases} for cadmium (0.9) (Figure 3) is a strong indication of the stability of the metal in the sediments. In general, cadmium in aquatic environments is found mainly in the solid phase, i.e. bottom sediments and suspended particles (Nordberg et al. 2007). If the pH of Nozha Hydrodrome water becomes more acidic (lower pH), the trapped zinc and cadmium are likely to be remobilized from the solid phase to the dissolved phase, thereby posing a hazard to the fauna and flora inhabiting the Hydrodrome.

6. Conclusions

Since 1900 zinc and cadmium have been accumulating in the bottom sediments of Nozha Hydrodrome. The temporal variations show that despite the expanding urbanization in the area, zinc in the sediments has been decreasing since 1990: untreated sewage is no longer discharged into the water since the sewer system and wastewater treatment plant came into operation. On the other hand, cadmium concentrations in the sediments have been increasing continuously during the past 100 years as a result of agricultural effluent being discharged into the pond. The reported concentrations of dissolved zinc and cadmium in Nozha Hydrodrome are low when compared with natural levels: this is an indication of the good quality

of its water and provides evidence that both metals are trapped in the solid phase (sediment and particulate matter).

Unless major changes in the physicochemical properties (especially pH) of the water take place, cadmium and zinc do not at present pose a serious environmental threat to the Nozha Hydrodrome ecosystem.

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